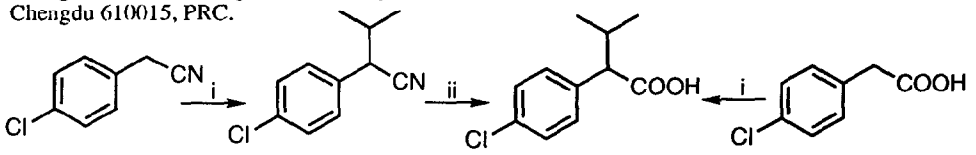
## GRAPHICAL ABSTRACTS

*Tetrahedron: Asymmetry* **1993**, *4*, 1957

Asymmetric Catalytic Alkylation of 4-Chlorophenylacetic Acid

A.Q. Mi, Z.Y. Wang and Y.Z. Jiang
Chengdu Institute of Organic Chemistry, Academia Sinica, P.O. Box 415, Chengdu 610015, PRC.

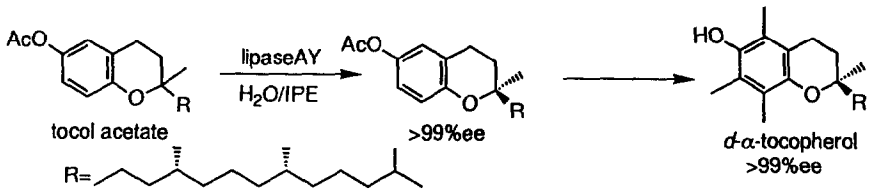



Scheme: Reagents i) chiral ligand, $^{i}$PrI, nBuLi, THF; ii) $H_2SO_4$, Δ; $CH_3COOH$

*Tetrahedron: Asymmetry* **1993**, *4*, 1961

**An Enzyme-catalyzed Synthesis of Natural α-Tocopherol**

Eisaku Mizuguchi,Masumi Takemoto,and Kazuo Achiwa*
*School of Parmaceutical Sciences,University of Shizuoka,52-1 Yada,Shizuoka422,Japan*



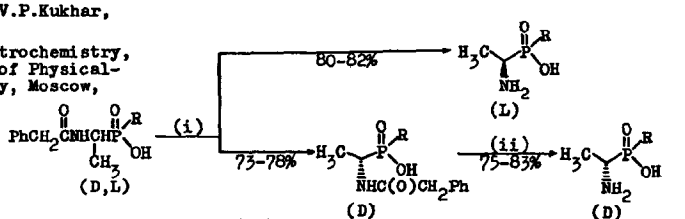

*Tetrahedron: Asymmetry* **1993**, *4*, 1965

**Enzymatic Preparation of Both L- and D-Enantiomers of Phosphonic and Phosphonous Analogues of Alanine Using Penicillin Acylase.**

V.A.Solodenko, M.Y.Belik, S.V.Galushko, V.P.Kukhar, E.V.Kozlova, D.A.Mironenko, V.K.Svedas.

Institute of Bioorganic Chemistry and Petrochemistry, Kiev, Ukraine; A.N.Belozersky Institute of Physical-Chemical Biology, Moscow State University, Moscow, Russia.

Step by step enzymatic hydrolysis of racemic 1-(N-phenylacetylamino)ethyl-phosphonic (-phosphonous) acids using penicillin acylase.

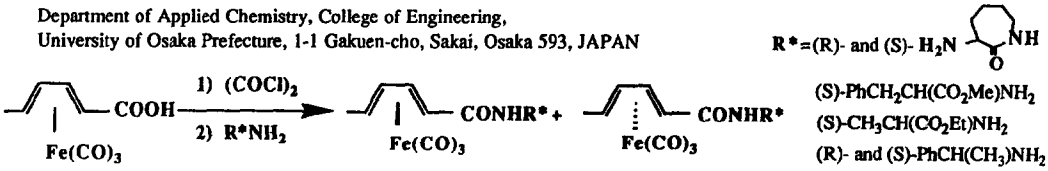



R = H, OH; (i) low enzyme concentration; (ii) high enzyme concentration

*Tetrahedron: Asymmetry* **1993**, *4*, 1969

**RESOLUTION AND CHARACTERIZATION OF DIASTEREOMERIC ($\eta^4$-DIENE)$Fe(CO)_3$ COMPLEXES CONTAINING CHIRAL AMIDE GROUPS**

S. Nakanishi,* H. Yamamoto, Y. Otsuji, and H. Nakazumi
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, 1-1 Gakuen-cho, Sakai, Osaka 593, JAPAN

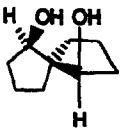


*Tetrahedron: Asymmetry* **1993**, *4*, 1973

## An Improved Synthesis and Resolution of (±)-*cis,cis*-Spiro[4.4]Nonane-1,6-Diol.

James A. Nieman, Masood Parvez and Brian A. Keay*
Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, T2N 1N4

(±)-*Cis,cis*-spiro[4.4]nonane-1,6-diol **2** is synthesized stereoselectively in four steps (51%) beginning with ethyl 2-oxocyclopentanecarboxylate. An improved resolution of diol **2** is described employing (1R)-(+)-camphor.



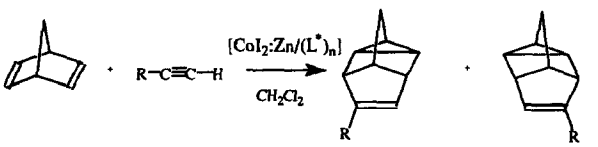

**2**

*Tetrahedron: Asymmetry* **1993**, *4*, 1977

## Enantioselective Synthesis of Deltacyclenes Using a [$CoI_2$:Zn] Catalytic System

Olivier Pardigon and Gérard Buono*
Ecole Nationale de Synthèses, Procédés et Ingénierie Chimiques d'Aix-Marseille (ENSSPICAM). URA 1410 Réactivité et catalyse, Faculté des Sciences et Techniques de St Jérôme, Université Aix-Marseille III, Avenue Escadrille-Niemen, 13397 Marseille Cedex 20, France.

Enantioselective [2+2+2] cycloadditions between norbornadiene and 1-alkynes lead to deltacyclenes with e.e.› 97% at room temperature.

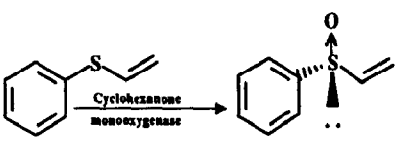



*Tetrahedron: Asymmetry* **1993**, *4*, 1981

## Asymmetric Oxidation of Sulfides by Cyclohexanone Monooxygenase

Francesco Secundo,[a] Giacomo Carrea,[a] Sabrina Dallavalle[b] and Giuliana Franzosi[c]
[a]Istituto di Chimica degli Ormoni, CNR, Milano, Italy. [b]Dipartimento di Chimica Organica e Industriale, Milano, Italy. [c]Istituto Donegani, Novara, Italy.

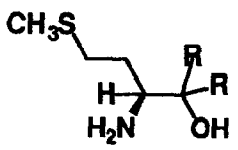
Cyclohexanone monooxygenase catalyzed the asymmetric oxidation of numerous alkyl aryl sulfides with the alkyl chain functionalized with Cl, CN, vinyl or hydroxy groups. Sulfoxides with ee up to 99% were obtained.




*Tetrahedron: Asymmetry* **1993**, *4*, 1983

## ENANTIOSELECTIVE CATALYTIC BORANE REDUCTIONS OF ACHIRAL KETONES; SYNTHESIS AND APPLICATION OF NEW CHIRAL β-AMINO ALCOHOLS FROM L-METHIONINE

Th. Mehler, J. Martens*
Fachbereich Chemie, Universität Oldenburg
Ammerländer Heerstr. 114-118, D-26129 Oldenburg




**1-3**

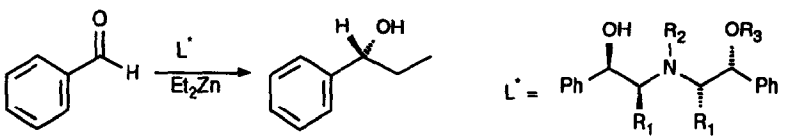
The optically active β-amino alcohols **1-3** (R = aryl) derived from (*S*)-methionine catalyze the enantioselective borane reduction of various achiral ketones to optically active secondary alcohols in up to 100 % *ee*.

*Tetrahedron: Asymmetry* **1993**, *4*, 1987

**Chiral Diethanolamines and their Lithium Alcoholates as Catalysts in the Enantioselective Alkylation of Benzaldehyde by Diethylzinc.**

Erik F. J. de Vries[1], Johannes Brussee[1], Chris G. Kruse[2] and Arne van der Gen[1]
1) Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands.
2) Solvay Duphar B.V., P.O. Box 900, 1380 DA, Weesp, The Netherlands.

The asymmetric addition of diethylzinc to benzaldehyde, catalyzed by chiral diethanolamines and their lithium alcoholates, was studied.

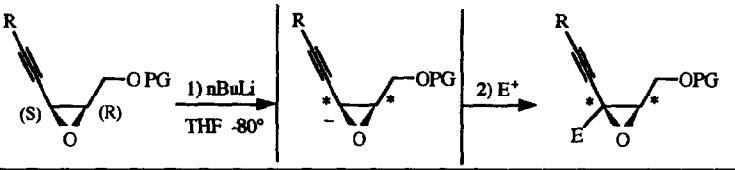



## SYNTHESIS OF OPTICALLY PURE TRISUBSTITUTED ETHYNYL OXIRANES BY OXIRANE DEPROTONATION

*Tetrahedron: Asymmetry* **1993**, *4*, 1991

D. Grandjean, P. Pale,* J. Chuche
Laboratoire de chimie organique physique, URA CNRS 459 Université de Reims-Champagne-Ardenne
51100 Reims, France.

Optically pure ethynyl oxiranes were easily deprotonated by nBuLi and the corresponding anions trapped by various electrophiles, providing a stereocontrolled access to optically pure trisubstituted ethynyl oxiranes.

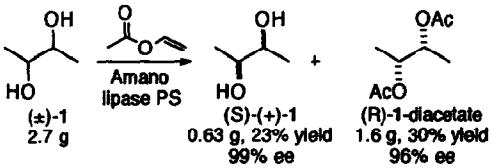



## SEQUENTIAL KINETIC RESOLUTION OF (±)-2,3-BUTANEDIOL IN ORGANIC SOLVENT USING LIPASE FROM *PSEUDOMONAS CEPACIA*.

*Tetrahedron: Asymmetry* **1993**, *4*, 1995

Gaétan Caron and Romas J. Kazlauskas,*
Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montréal, Québec H3A 2K6, Canada

Lipase from *Pseudomonas cepacia* (PCL, Amano PS) catalyzed the enantioselective diacetylation of (±)-2,3-butanediol in vinyl acetate. Both acetylation steps favored the (R)-enantiomer ($E_1 = 12$, $E_2 = 34$), thus the reaction is a sequential kinetic resolution with an overall enantioselectivity of approximately 200.

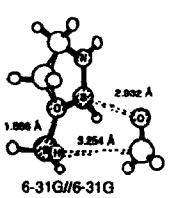



*Tetrahedron: Asymmetry* **1993**, *4*, 2001

Quantum Chemical Modeling of Chiral Catalysis. Part 13. On the Role of Borane *O*-Adducts in the Enantioselective Reduction of Ketones Catalyzed by Chiral Oxazaborolidines

Vesa Nevalainen, Division of Organic Chemistry, P.O. Box 6, SF-00014 University of Helsinki, Finland

*Abstract:* - Plausible reactions of Lewis bases (ketones and ethers) with borane *O*-adducts of chiral oxazaborolidines used as catalysts in the enantioselective reduction of ketones were investigated by means of *ab initio* MO methods. Properties of the *O*-adducts were found to be different from those of the corresponding *N*-adducts. The *O*-adducts were not able to form complexes with ketones and ethers similar to those of the corresponding *N*-adducts. Distances between the Lewis acidic and basic centers were much longer in the *O*-adducts than in the corresponding *N*-adducts.



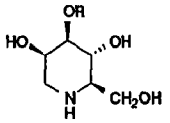
6-31G//6-31G

*Tetrahedron: Asymmetry* **1993**, *4*, 2011

## Synthesis of 1,5-Dideoxy-3-O-(α-D-mannopyranosyl)-1,5-imino-D-mannitol and 1,5-Dideoxy-3-O-(α-D-glucopyranosyl)-1,5-imino-D-mannitol: Powerful Inhibitors of an endoMannosidase

H. Ardron,[a] T. D. Butters,[b] F. M. Platt,[b] M. R. Wormald,[b] R. A. Dwek,[b] G. W. J. Fleet[a]* and G. S. Jacob[c]
[a]Dyson Perrins Laboratory, Oxford Centre for Molecular Sciences, South Parks Road, Oxford OX1 3QY UK
[b]Glycobiology Institute, Biochemistry Department, Oxford University, South Parks Road, Oxford OX1 3QU UK; [c]Monsanto Company, 800, North Lindbergh Boulevard, St Louis, Missouri 63167, U S A

Glcα1,3DMJ and Manα1,3DMJ are potent inhibitors of an endomannosidase



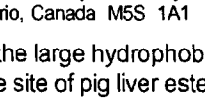

R= α-D-glucopyranosyl Glcα1,3DMJ
R= α-D-mannopyranosyl Manα1,3DMJ

*Tetrahedron: Asymmetry* **1993**, *4*, 2025

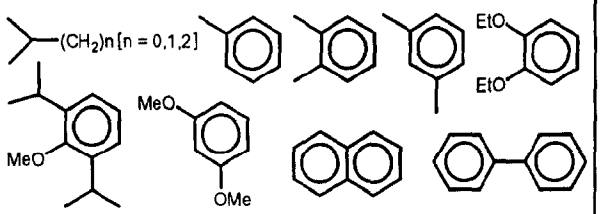
## Enzymes in Organic Synthesis 51. Probing the Dimensions of the Large Hydrophobic Region of the Active Siteof Pig Liver Esterase

Louis Provencher, Hla Wynn, J. Bryan Jones
Department of Chemistry, University of Toronto
Toronto, Ontario, Canada M5S 1A1

The size of the large hydrophobic pocket of the active site of pig liver esterase has been further probed using substrates



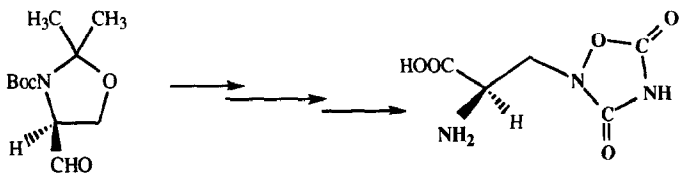

R=




*Tetrahedron: Asymmetry* **1993**, *4*, 2041

## Enantiospecific synthesis of quisqualic acid

C. Guibourdenche, M.L. Roumestant, Ph. Viallefont
URA 468, UM II, 34095 Montpellier Cedex 5




2S-Aldehyde

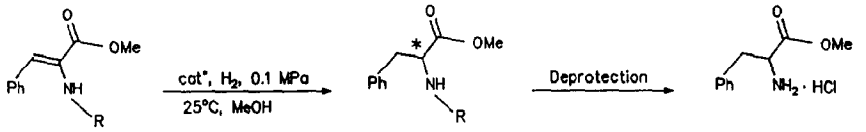
2R-Quisqualic acid

*Tetrahedron: Asymmetry* **1993**, *4*, 2047

## ASYMMETRIC HYDROGENATION OF (Z)-N-ACYLAMINOCINNAMIC ACID DERIVATIVES

H.-J. Kreuzfeld, Chr. Döbler, H.W. Krause
Institut für Organische Katalyseforschung, D-18055 Rostock

The influence of N-protected aminocinnamic acid methyl esters, bearing different protective groups (Ac, Bz, Cbz, Boc), on the rate and enantioselectivity has been investigated in the presence of four catalysts.

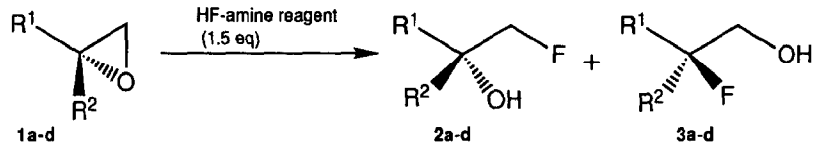



R = Ac, Bz, Cbz, Boc

*Tetrahedron: Asymmetry* **1993**, *4*, 2053

**Stereo- and Regiocontrolled Synthesis of Fluorohydrins from Optically Active Epoxides.**

Junko Umezawa,* Osamu Takahashi, Keizo Furuhashi, and Hiroyuki Nohira
Department of Applied Chemistry, Faculty of Engineering, Saitama University, Shimo-ohkubo, Urawa, Saitama 338, Japan



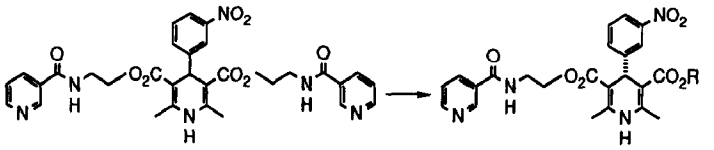

**1a** : $R^1$=n-$C_6H_{13}$, $R^2$=H
**1b** $R^1$=n-$C_6H_{13}OCH_2$, $R^2$=H
**1c** : $R^1$=n-$C_4H_9$, $R^2$=$CH_3$
**1d** : $R^1$=$C_6F_5$, $R^2$=H

*Tetrahedron: Asymmetry* **1993**, *4*, 2061

Chemoenzymatic Synthesis of Optically Active 1,4-Dihydropyridine Derivatives via Enantioselective Hydrolysis and Transesterification

Takashi Adachi, Mayumi Ishii, Yoko Ohta, Tomomi Ota, Toshihisa Ogawa and Kazunori Hanada
Research Center, Taisho Pharmaceutical Co., Ltd., 1-403 Yoshino-cho, Ohmiya-shi, Saitama 330, Japan

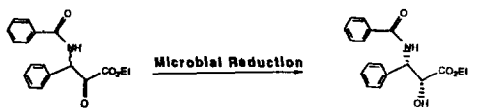
Optically active 1,4-dihydropyridine derivatives were synthesized via both enantioselective hydrolysis and transesterification of a prochiral diester by using protease originated from *Aspergillus melleus*.




*Tetrahedron: Asymmetry* **1993**, *4*, 2069

**Microbial Synthesis of (2R,3S)-(-)-N-Benzoyl-3-phenyl Isoserine ethyl ester, a taxol side-chain synthon**

Ramesh N. Patel*, Amit Banerjee, Jeffrey M. Howell, Clyde G. McNamee, David Brozozowski, David Mirfakhrae, Venkat Nanduri, John K. Thottathil, and Laszlo J. Szarka
Department of Microbial Technology and Chemical Process Research, Bristol-Myers Squibb Pharmaceutical Research Institute, P. O. Box 191, New Brunswick, N. J. 08903

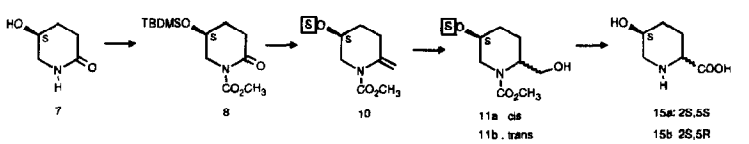



Hansenula polymorpha SC 13865 was used to prepare (2R,3S)-(-)-N-Benzoyl-3-phenyl isoserine ethyl ester, a taxol side-chain synthon

*Tetrahedron: Asymmetry* **1993**, *4*, 2085

**Synthesis of (2S,5S)-5-Hydroxypipecolic Acid via Amide-Methylenation of S-5-Hydroxy-2-piperidone with Dimethyltitanocene**

**Claus Herdeis and Eberhard Heller**
**Institut für Pharmazie und Lebensmittelchemie der Universität, Am Hubland D-97074 Würzburg**

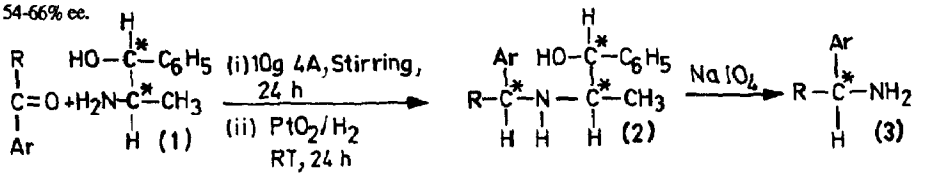


*Tetrahedron: Asymmetry* **1993**, *4*, 2095

## CHIRAL SYNTHESIS OF AMINES BY THE REDUCTIVE AMINATION OF KETONES USING (+) AND (-) NOREPHEDRINE FOLLOWED BY PERIODATE OXIDATION

R. Sreekumar and C. N. Pillai,* Department of Chemistry, Indian Institute of Technology, Madras, India.

Aralkyl ketone was condensed with chiral norephedrine (**1**), the resulting Schiff base was hydrogenated using Adams catalyst. The chiral β-aminoalcohol (**2**) was oxidized by periodic acid to obtain chiral aralkyl primary amine (**3**) in 54-66% ee.




*Tetrahedron: Asymmetry* **1993**, *4*, 2101

## 2- AND 8- FUNCTIONALIZED 1,4,7,10-TETRAOXASPIRO[5.5]UNDECANES.II. Synthesis of (+)-E,E and (±)-Z,E structures from chiral isopropylideneglycerols.

M. Lemaire, G. Jeminet, J.-G. Gourcy and G. Dauphin Université Blaise Pascal, URA 485 du CNRS. Laboratoire de chimie Organique Biologique, 63177 Aubière Cedex, France

Deprotection-cyclisation of ketones 5 and 12 gave respectively the pure E,E-(+) enantiomer **6** and the racemic mixture Z,E-(±) **13**.